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PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7 :
C08L 15/00, C08K 3/36, B60C 1/00

A1

(11) International Publication Number: WO 00/37555

(43) International Publication Date: 29 June 2000 (29.06.00)

(21) International Application Number: PCT/EP99/09646

(22) International Filing Date: 6 December 1999 (06.12.99)

(30) Priority Data:

98124373.6	22 December 1998 (22.12.98)	EP
60/116,237	15 January 1999 (15.01.99)	US

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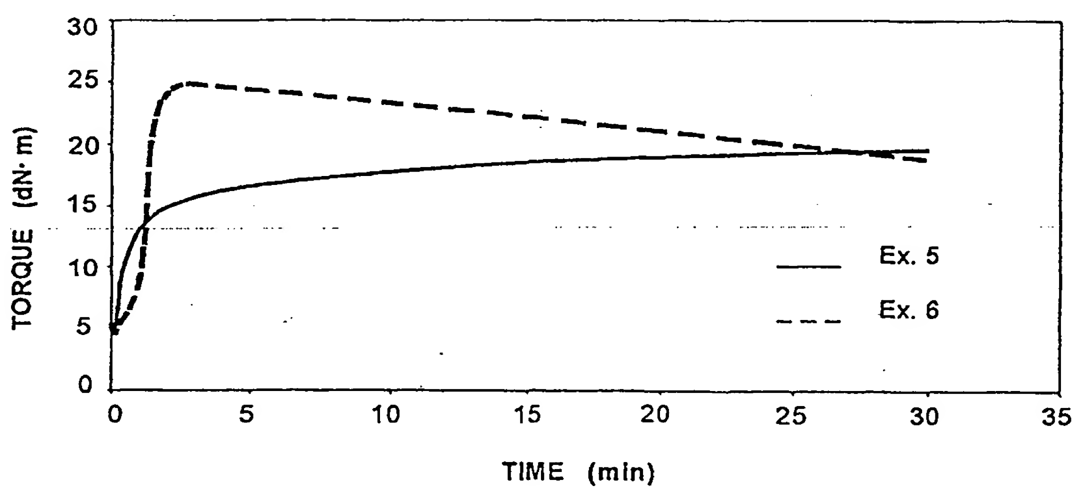
(81) Designated States: BR, CN, ID, JP, KR, RU, TR, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: PROCESS FOR PRODUCING TYRES, TYRES THUS OBTAINED AND ELASTOMERIC COMPOSITIONS USED THEREIN



(57) Abstract

Process for producing tyres for the wheels of vehicles, in which the raw tyre comprises at least one crosslinkable elastomeric material comprising an elastomeric polymer containing epoxide groups and an active filler containing hydroxyl groups dispersed in the said polymer, the said elastomeric material being crosslinked essentially without additional crosslinking agents. The elastomeric material is characterized by an effective degree of crosslinking equal to at least 65 % after not more than 5 min of heating at 170 °C.

PROCESS FOR PRODUCING TYRES, TYRES THUS OBTAINED AND ELASTOMERIC COMPOSITIONS USED THEREIN

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The present invention relates to a process for producing tyres for the wheels of vehicles, to the tyres thus obtained and to crosslinkable elastomeric compositions used therein. More particularly, the present invention relates to a process for producing tyres for the wheels of vehicles, which can be made essentially without conventional crosslinking agents, to the tyres thus obtained and to the crosslinkable compositions used therein comprising a polymer containing epoxide groups and an active filler containing hydroxyl groups.

Processes for vulcanizing diene elastomers with sulphur are widely used in the rubber industry for the production of a wide range of products, and in particular tyres for the wheels of vehicles. Although these processes give high-quality vulcanized products, they are considerably complicated to carry out, mainly due to the fact that, in order to obtain optimum vulcanization within industrially acceptable times, it is necessary to use a complex vulcanizing system which includes, besides sulphur or sulphur-donating compounds, one or more activators (for example stearic acid, zinc oxide and the like) and one or more accelerators (for example thiazoles, dithiocarbamates, thiurams, guanidines, sulphenamides and the like). The presence of these products can, in some cases, entail considerable problems in terms of

the harmfulness/toxicity both during production and during use, in particular when the vulcanized products are intended for medical/health-care or food use. In addition, it is known that the use of sulphur or sulphur-donating compounds leads, during the vulcanization stage which is generally carried out at temperatures above 150°C, to the development of volatile sulphurized compounds.

Consequently, in recent years, research efforts have been directed along two different lines, the first being to improve the known vulcanization processes in order to make them more efficient and cleaner, the second aimed at developing alternative crosslinking techniques. Although appreciable progress has been made, it is not possible to state at the present time that alternative techniques to crosslinking with sulphur exist which would give similar results and would simultaneously afford an effective simplification in terms of production. For example, crosslinking processes mediated by peroxide compounds require special precautions on account of the instability of these compounds, in addition to requiring the use of activators. Radiation-mediated crosslinking involves the use of complex equipment, as well as the incorporation of all the precautions required when high-energy and high-power radiation is used.

It is known practice to produce tyres for the wheels of vehicles using elastomeric compositions containing silica or mixtures of silica and carbon

black as reinforcing filler. These compositions are usually used to produce tyre tread bands which display excellent roadholding, in particular in wet conditions, and low resistance to rolling. To this end, blends containing silica or silica/carbon black mixtures and, as polymer base, a polymer containing epoxide groups, for example epoxidized natural rubber or an epoxidized styrene/butadiene copolymer (see, for -example, patents US-4,179,421, US-4,341,672, EP-644,235 and EP-763,564), have been developed in particular. These blends are crosslinked according to conventional methods, in particular by means of systems with sulphur or peroxides. Silane compounds are usually added to the blends in order to increase the compatibility between the silica and the polymer base.

The article by S. Varughese and D.K.Tripathy published in the *Journal of Applied Polymer Science*, Vol. 44, pp. 1847-1852 (1992) reports a study on the rheometric behaviour of blends consisting of epoxidized natural rubber (ENR) and silica which are free of conventional crosslinking agents, in order to investigate the interactions between ENR and silica. In particular, blends containing ENR epoxidized to 50 mol% (ENR-50), silica and optionally bis(triethoxy-silylpropyl) tetrasulphide (Si-69) as compatibilizing agent were prepared. The blends were prepared in a laboratory two-cylinder mixer using as short a mixing time as possible in order to avoid adhesion of the blends to the mixer cylinders. The

rheological properties were studied using a rheometer heated at 180°C for 1 hour. According to the authors, the results obtained are said to demonstrate that a chemical reaction takes place between the silica and the ENR-50, leading to mild crosslinking. A slightly higher level of crosslinking is said to be obtainable in the samples containing silane.

From the rheometric curves reported in the abovementioned article, a modest rise can indeed be seen in the torque values (evaluated by the Applicant at about 5 dN·m after 1 hour of heating at 180°C - see page 1849, Figure 1, Curve D) with a quite modest rate. These values thus appear to indicate the existence of a certain degree of crosslinking in the blends containing silica and ENR-50, but it is of modest extent and above all has an extremely low rate of crosslinking, which is entirely insufficient for them to be of practical use. This fact is confirmed by the same authors of the article mentioned above, when they state that the assumed crosslinking between the epoxide groups and the silanol groups in the silica would require an activation energy greater than that in common vulcanization processes (see page 1849). Thus, these blends would be entirely unsuitable for the industrial-scale production of crosslinked elastomeric manufactured products in general, and specifically of tyres.

The Applicant has now found, surprisingly, that crosslinked manufactured products, and in particular tyres for the wheels of vehicles, can be produced,

essentially without additional crosslinking agents, by using crosslinkable compositions comprising an elastomeric polymer containing epoxide groups and an active filler containing hydroxyl groups. By heating to a predetermined temperature and for a predetermined time, these compositions achieve a high degree of crosslinking in short times, thereby enabling them to be used for the industrial-scale production of crosslinked manufactured products, and in particular of tyres.

According to a first aspect, the present invention thus relates to a process for producing tyres for the wheels of vehicles, the said process comprising the following phases:

- making a raw tyre comprising at least one crosslinkable elastomeric material;
- molding the raw tyre in a molding cavity defined in a vulcanization mold;
- crosslinking the elastomeric material by heating the tyre to a predetermined temperature and for a predetermined time;

characterized in that the raw tyre comprises at least one crosslinkable elastomeric material comprising an elastomeric polymer containing epoxide groups and an active filler containing hydroxyl groups which is dispersed in the said polymer, and in that the phase of crosslinking of the said elastomeric material is carried out essentially without additional crosslinking agents.

According to a preferred aspect, the crosslinking phase is carried out by heating the tyre to a maximum temperature of at least 100°C, preferably of at least 120°C, for a time of at least 3 minutes, preferably of at least 5 minutes.

According to a further preferred aspect, the active filler is dispersed in the elastomeric polymer containing epoxide groups, with a dispersion index of greater than 90%, preferably greater than 95%, even more preferably greater than 98%.

According to a further preferred aspect, the crosslinkable elastomeric material is characterized by an effective degree of crosslinking equal to at least 65% after no more than 5 minutes of heating at 170°C.

In a second aspect, the present invention relates to a tyre for the wheels of vehicles, comprising one or more components made of crosslinked elastomeric material, characterized in that at least one of the said components comprises an elastomeric polymer containing epoxide groups and an active filler containing hydroxyl groups which is dispersed in the said polymer, the said material being crosslinked essentially without additional crosslinking agents.

According to a further aspect, the present invention relates to a composition comprising an elastomeric polymer containing epoxide groups and an active filler containing hydroxyl groups which is dispersed in the said polymer, the said composition being crosslinkable essentially without additional

crosslinking agents and being characterized by an effective degree of crosslinking equal to at least 65% after no more than 5 minutes of heating at 170°C.

According to a further aspect, the present invention relates to a crosslinked manufactured product comprising an elastomeric polymer containing epoxide groups and an active filler containing hydroxyl groups which is dispersed in the said polymer, characterized in that the said manufactured product is crosslinked essentially without additional crosslinking agents, and the filler is dispersed in the polymer, with a dispersion index of greater than 90%, preferably greater than 95%, even more preferably greater than 98%.

According to a further aspect, the present invention relates to a process for preparing an elastomeric composition comprising an elastomeric polymer containing epoxide groups and an active filler containing hydroxyl groups which is dispersed in the said polymer, the said composition being crosslinkable without additional crosslinking agents, the said process comprising mixing the active filler with the polymer for a predetermined time so as to obtain a degree of dispersion of the filler of greater than 90%, and at a predetermined temperature so as to avoid pre-crosslinking of the composition.

For the purposes of the present description and the claims, the expression "essentially without additional crosslinking agents" means that the crosslinkable composition is not subjected to the

action of other systems capable of bringing about the crosslinking, or else that other products which may be present in the composition can in themselves participate in the crosslinking reaction, but are used in amounts less than the minimum amount required to obtain an appreciable degree of crosslinking in short times (for example within 5 minutes). In particular, the compositions according to the present invention are crosslinkable essentially without any of the crosslinking systems usually used in the art, such as, for example, sulphur or sulphur donors, peroxides or other radical initiators, and neither are these compositions subjected to the action of high-energy radiation (UV, gamma rays, etc.) so as to induce crosslinking phenomena in the polymer.

For the purposes of the present description and the claims, the expression "effective degree of crosslinking" ($\%R_{eff}$) means, with reference to an MDR (MDR = moving die rheometer) rheometric curve obtained on a sample of the composition heated at 170°C for a total time of 30 min, the difference between the effective torque (M_{eff}) and the minimum torque (M_L) values, which is expressed as a percentage relative to the difference between the final torque (M_{fin}), i.e. at the time t_{fin} = 30 min, and M_L:

$$\%R_{eff} = \frac{M_{eff} - M_L}{M_{fin} - M_L} * 100 \qquad (1)$$

The M_{eff} value is unambiguously determined from the MDR curve as the torque value at the point of intersection between:

- the line (A) which passes between the minimum point on the MDR curve (t_{ML}; M_L) and the point at which there is an increase of 1 dN·m in the torque value relative to M_L (t_{s1}; M_L+1); and:
- the line (B) which passes between the final point (30; M_{fin}) and the point at which there is an increase in the torque value relative to M_L equal to 90% of the total variation of the torque between the maximum value M_H and the minimum value M_L (t_{90}; $M_L + 0.9 (M_H - M_L)$).

The gradients of the lines (A) and (B) represent a measure, respectively, of the mean initial cross-linking speed (i.e. in the first period after the minimum point M_L at which the crosslinking has started) and the mean final crosslinking speed (i.e. in the period between the point at which 90% of the total crosslinking is obtained and the final point, set at 30 min).

Fig. 1 is a typical MDR curve on which the characteristic points and the lines (A) and (B) are shown.

The following equations (2) and (3) represent the lines A and B, respectively:

$$M = v_i{*}t + (M_L + 1) - v_i{*}t_{s1} \qquad (2)$$

$$M = v_f{*}t + M_{fin} - v_f{*}30 \qquad (3)$$

where M_L, t_{s1} and M_{fin} are defined above, while:

$$V_i = \frac{1}{t_{s1} - t_{ML}} \quad (4)$$

$$V_f = \frac{M_{fin} - (M_L + 0.9(M_H - M_L))}{30 - t_{90}} \quad (5)$$

Equating equations (2) and (3) gives the expression which makes it possible to calculate t_{eff} and thus M_{eff}:

$$t_{eff} = \frac{M_{fin} - (M_L + 1) - V_f * 30 + V_i * t_{s1}}{V_i - V_f} \quad (6)$$

$$M_{eff} = V_i * t_{eff} + (M_L + 1) - V_i * t_{s1} \quad (7)$$

The MDR curves can be determined as described in ASTM standard D5289-95.

The polymers containing epoxide groups which can be used in the compositions according to the present invention are homopolymers or copolymers with elastomeric properties, having a glass transition temperature (T_g) of less than 23°C, preferably less than 0°C, containing at least 0.05 mol%, preferably from 0.1 to 70 mol%, even more preferably from 0.5 to 60 mol%, of epoxide groups relative to the total number of moles of monomers present in the polymer. Mixtures of different polymers containing epoxide groups, or alternatively mixtures of one or more epoxidized polymers with one or more non-epoxidized elastomeric polymers, also fall within this definition.

In the case of copolymers, these can have a random, block, grafted or mixed structure. The average molecular weight of the base polymer is preferably between 2000 and 1,000,000, preferably between 50,000 and 500,000.

In particular, epoxidized diene homopolymers or copolymers, in which the base polymer structure, of synthetic or natural origin, is derived from one or more conjugated diene monomers, optionally copolymerized with monovinylarenes and/or polar comonomers, are preferred.

The polymers which are particularly preferred are those derived from the (co)polymerization of diene monomers containing from 4 to 12, preferably from 4 to 8, carbon atoms, chosen, for example, from: 1,3-butadiene, isoprene, 2,3-dimethyl-1,3-butadiene, 3-butyl-1,3-octadiene, 2-phenyl-1,3-butadiene and the like, or mixtures thereof. 1,3-Butadiene and isoprene are particularly preferred.

Monovinylarenes which can optionally be used as comonomers generally contain from 8 to 20, preferably from 8 to 12, carbon atoms and can be chosen, for example, from: styrene; 1-vinylnaphthalene; 2-vinylnaphthalene; various alkyl, cycloalkyl, aryl, alkylaryl or arylalkyl derivatives of styrene, such as, for example: 3-methylstyrene, 4-propylstyrene, 4-cyclohexylstyrene, 4-dodecylstyrene, 2-ethyl-4-benzylstyrene, 4-p-tolylstyrene, 4-(4-phenylbutyl)styrene and the like, or mixtures thereof. Styrene is particularly preferred. These

monovinylarenes can optionally be substituted with one or more functional groups, such as alkoxy groups, for example 4-methoxystyrene, amino groups, for example 4-dimethylaminostyrene, and the like.

Various polar comonomers can be introduced into the base polymer structure, in particular vinylpyridine, vinylquinoline, acrylic and alkylacrylic acid esters, nitriles and the like, or mixtures thereof, such as, for example: methyl acrylate, ethyl acrylate, methyl methacrylate, ethyl methacrylate, acrylonitrile and the like.

Among the diene polymers which are particularly preferred are: natural rubber, polybutadiene, polyisoprene, styrene/butadiene copolymers, butadiene/isoprene copolymers, styrene/isoprene copolymers, nitrile rubbers and the like, or mixtures thereof.

In the case of copolymers, the amount of diene comonomer relative to the other comonomers is such as to ensure that the final polymer has elastomeric properties. In this sense, it is not possible generally to establish the minimum amount of diene comonomer required to obtain the desired elastomeric properties. As a guide, an amount of diene comonomer of at least 50% by weight relative to the total weight of the comonomer can generally be considered sufficient.

The base diene polymer can be prepared according to known techniques, generally in emulsion, in suspension or in solution. The base polymer thus

obtained is then subjected to epoxidization according to known techniques, for example by reaction in solution with an epoxidizing agent. This agent is generally a peroxide or a peracid, for example m-chloroperbenzoic acid, peracetic acid and the like, or hydrogen peroxide in the presence of a carboxylic acid or a derivative thereof, for example acetic acid, acetic anhydride and the like, optionally mixed with an acid catalyst such as sulphuric acid. Further details regarding processes for epoxidizing elastomeric polymers are described, for example, in US patent 4,341,672 or by Schulz et al. in *Rubber Chemistry and Technology*, Vol. 55, p. 809 et seq.

Polymers containing epoxide groups which can also be used are elastomeric copolymers of one or more monoolefins with an olefinic comonomer containing one or more epoxide groups. The monoolefins can be chosen from: ethylene and α-olefins generally containing from 3 to 12 carbon atoms, such as, for example: propylene, 1-butene, 1-pentene, 1-hexene, 1-octene and the like, or mixtures thereof. The following are preferred: copolymers between ethylene and an α-olefin, and optionally a diene; homopolymers of isobutene or copolymers thereof with smaller amounts of a diene, which are optionally at least partially halogenated. The diene optionally present generally contains from 4 to 20 carbon atoms and is preferably chosen from: 1,3-butadiene, isoprene, 1,4-hexadiene, 1,4-cyclohexadiene, 5-ethylidene-2-norbornene, 5-methylene-2-norbornene and the like. Among these,

the following are particularly preferred: ethylene/propylene copolymers (EPR) or ethylene/propylene/diene copolymers (EPDM); polyisobutene; butyl rubbers; halobutyl rubbers, in particular chlorobutyl or bromobutyl rubbers; and the like, or mixtures thereof. Olefinic comonomers containing epoxide groups can be chosen, for example, from: glycidyl acrylate, glycidyl methacrylate, vinylcyclohexene monoxide, allyl glycidyl ether and methallyl glycidyl ether. The introduction of the epoxide groups by the abovementioned epoxidized comonomers can be carried out by copolymerization of the corresponding monomers according to known techniques, in particular by radical copolymerization in emulsion. When a diene comonomer is present, this can be used to introduce epoxide groups by an epoxidation reaction as described above.

Examples of epoxidized elastomeric polymers which can be used in the present invention and which are currently commercially available are the products Epoxyprene® from Guthrie (epoxidized natural rubber - ENR) and the products Poly BD® from Elf Atochem (epoxidized polybutadiene).

For the purposes of the present invention, the expression "active filler containing hydroxyl groups" means a material of inorganic or organic nature in subdivided form whose surface bears active hydroxyl groups capable of interacting with the epoxide groups of the polymer. The following materials, for example, fall into this class: silica, in particular

precipitated silica and pyrogenic silica, alumina, titanium oxide, cellulose fibres, microcrystalline cellulose, zeolites, kaolin and the like, or mixtures thereof. It is also possible to use fillers, which are not active per se, whose surface is modified with hydroxyl groups, for example carbon black at least partially coated with silica, as described, for example, in patent application WO 96/37546 and WO 98/13428.

Active fillers which are particularly preferred are: precipitated silica, pyrogenic silica, alumina or mixtures thereof. In order to obtain effective interaction with the epoxidized polymer, the surface area of the active filler (determined by the BET method) is preferably greater than 40 m^2/g, even more preferably between 80 and 600 m^2/g, while the density of the active hydroxyl groups present on the filler is generally greater than 1 group/nm^2, preferably greater than 5 groups/nm^2. The density of active hydroxyl groups can be determined by NMR analysis, as described, for example, by Leonardelli et al. in J. Am. Chem. Soc., 114, 16 (1992).

In particular, commercial products which can advantageously be used as active fillers according to the present invention can be chosen, for example, from: VN3 products from Degussa, Zeosil® products from Rhône-Poulenc and Ecoblack® products from Cabot Corp.

The minimum amount of filler required to obtain a satisfactory degree of crosslinking can be determined

as a function of the specific materials used and the characteristics which it is desired to obtain for the final crosslinked manufactured product. On the basis of the investigations carried out, the Applicant has found that, in general, it is necessary to use an amount of active filler of greater than 20 phr, preferably between 30 and 150 phr (phr = parts by weight per 100 parts by weight of polymer base).

The active filler can be used as a mixture with other non-active fillers commonly used as reinforcers in crosslinked elastomeric compositions, for example carbon black, calcium carbonate and the like. It is found that an amount of active filler equal to at least 50% by weight of the total weight of filler present in the blend is sufficient to obtain a satisfactory result. Naturally, these amounts can vary as a function of the nature of the fillers used and the characteristics required for the final crosslinked manufactured product.

The dispersion index (D%) of the active filler in the polymer base can be determined by optical or electron microscopy analysis of a thin section (thickness: 1 µm) of the composition on the basis of the number of particles of undispersed filler. Conventionally, filler which is aggregated in the form of particles with a diameter of greater than or equal to 7 µm is considered as "undispersed".

The dispersion index is calculated according to the following formula:

$$D\% = (1 - 0.4 * \frac{V}{L}) * 100 \qquad (8)$$

where:

$$V = \frac{A}{A_{tot}} * 100 \qquad (9)$$

$$L = \frac{d_c}{d_f} * F\% \qquad (10)$$

A = total area of the undispersed particles;
A_{tot} = total area of the section examined;
d_c = density of the composition;
d_f = density of the filler;
%F = % by weight of filler present in the composition.

The factor 0.4 in formula (8), usually known as the "swelling factor", is a parameter of empirical nature which gives a measure of the amount of filler effectively present in the undispersed aggregates, taking into account the fact that a certain amount of "trapped" polymer is present in these aggregates. When the filler per se cannot readily be distinguished from the surrounding polymer matrix, in particular when an optical microscope is used, a small amount of a suitable contrast agent, for example carbon black, can be added to the filler.

Further details regarding the determination of the dispersion index of the filler are given, for example, in: "Carbon Black Dispersion Measurement.

Part II. Influence of Dispersion on Physical Properties" by B.R. Richmond (Meeting of the Rubber Division, ACS, October 26-29, 1993).

The crosslinkable compositions according to the present invention can comprise additives commonly used, chosen on the basis of the specific application for which they are intended. For example, antioxidants, protective agents, plasticizers, adhesives, anti-ozonizing agents, curing resins, modifying resins, fibres (for example Kevlar® pulp), and the like, can be added to these compositions. In particular, in order to improve the processability, a lubricant, generally chosen from mineral oils, plant oils, synthetic oils and the like, or mixtures thereof, for example: aromatic oil, naphthenic oil, phthalates, soybean oil, epoxidized soybean oil and the like, can be added to the crosslinkable compositions according to the present invention. The amount of lubricant can generally range between 2 and 100 phr, preferably between 5 and 50 phr.

The crosslinkable compositions according to the present invention can be prepared by mixing the polymer base and the active filler according to techniques known in the art. The mixing can be carried out, for example, using an open-mill mixer, or an internal mixer of the type with tangential rotors (Banbury) or interlocking rotors (Intermix), or in continuous mixers of the Ko-Kneader (Buss) or co-rotating or counter-rotating twin-screw type.

During the mixing, the temperature is kept below a predetermined value so as to avoid premature cross-linking of the composition. To this end, the temperature is generally kept below 130°C, preferably below 100°C, even more preferably below 80°C. As regards the mixing time, this can vary within a wide range, depending mainly on the specific composition of the blend and on the type of mixer used, and is predetermined so as to obtain the desired degree of dispersion of the filler in the polymer base. In general, a satisfactory result can be obtained with a mixing time of more than 90 sec, preferably between 3 and 35 min.

In order to optimize the dispersion of the filler while keeping the temperature below the values indicated above, multi-stage mixing processes can also be employed, optionally using a combination of different mixers arranged in series.

As an alternative to the abovementioned solid-state mixing processes, in order to avoid problems deriving from an overheating of the blend with consequent undesired pre-crosslinking phenomena, the crosslinkable compositions according to the present invention can advantageously be prepared by mixing the active filler with the polymer base in the form of an aqueous emulsion or a solution in an organic solvent. The filler can be used as it is or in the form of a suspension or dispersion in an aqueous medium. The polymer thus filled is subsequently separated from the solvent or from the water by

suitable means. For example, when a polymer in emulsion is used, the polymer can be precipitated in the form of particles including the filler by adding a coagulant.

A coagulant which can be used, in particular is an electrolytic solution, for example an aqueous sodium or potassium silicate solution. The coagulation process can be promoted by using a volatile organic solvent which is then removed by evaporation during precipitation of the filled polymer. Further details regarding processes of this type for the preparation of filled elastomers are given, for example, in US patent 3,846,365.

The present invention will now be further illustrated by a number of embodiments, with reference to the attached figures, in which:

Figure 1 is a view in cross section with partial cutaway of a tyre according to the present invention;

Figure 2 shows a typical MDR curve, in which are given the critical points and the lines (A) and (B) as defined above;

Figure 3 shows the MDR curves obtained for Examples 5 and 6 given later.

With reference to Fig. 1, a tyre 1 conventionally comprises at least one carcass ply 2 whose opposite side edges are externally folded around respective anchoring bead cores 3, each enclosed in a bead 4 defined along an inner circumferential edge of the tyre, with which the tyre engages on a rim 5 forming part of the wheel of a vehicle.

Along the circumferential development of the carcass ply 2 are applied one or more belt strips 6, made using metal or textile cords enclosed in a sheet of blend. Outside the carcass ply 2, in respective opposite side portions of this ply, there is also applied a pair of sidewalls 7, each of which extends from the bead 4 to a so-called "shoulder" region 8 of the tyre, defined by the opposing ends of the belt strips 6. On the belt strips 6 is circumferentially applied a tread band 9 whose side edges end at the shoulders 8, joining it to the sidewalls 7. The tread band 9 externally has a rolling surface 9a, designed to come into contact with the ground, in the surface of which tread band can be made circumferential grooves 10 intercalated with transverse grooves, not shown in the attached figure, which define a plurality of blocks 11 variously distributed on the said rolling surface 9a.

The process for producing the tyre according to the present invention can be carried out according to techniques and using apparatus known in the art (see, for example, patents EP 199,064, US 4,872,822 and US 4,768,937). More particularly, this process comprises a phase of manufacturing the raw tyre, in which a series of semi-finished articles, prepared beforehand and separately from each other and corresponding to the various parts of the tyre (carcass plies, belt strips, bead hoops, fillers, sidewalls and tread) are combined together using a suitable manufacturing machine.

The raw tyre thus obtained is then subjected to the subsequent phases of molding and crosslinking. To this end, a vulcanization mold is used which is designed to receive the tyre being processed inside a molding cavity having walls which are countermolded to the outer surface of the tyre when the crosslinking is complete.

The raw tyre can be molded by introducing a pressurized fluid into the space defined by the inner surface of the tyre, so as to press the outer surface of the raw tyre against the walls of the molding cavity. In one of the molding methods widely practised, it is envisaged that a vulcanization chamber made of elastomeric material, filled with steam and/or another fluid under pressure, is expanded inside the tyre closed inside the molding cavity. In this way, the raw tyre is pushed against the inner walls of the molding cavity, thus obtaining the desired molding. Alternatively, the molding can be carried out without an expandable vulcanization chamber, by providing inside the tyre a toroidal metal support shaped according to the configuration of the inner surface of the tyre to be obtained (see, for example, patent EP 242,840). The difference in coefficient of thermal expansion between the toroidal metal support and the crude elastomeric material is exploited to achieve an adequate molding pressure.

At this point, the phase of crosslinking of the raw elastomeric material present in the tyre is carried out. To this end, the outer wall of the

vulcanization mold is placed in contact with a heating fluid (generally steam) such that the outer wall reaches a maximum temperature generally of between 100°C and 200°C. Simultaneously, the inner surface of the tyre is brought to the crosslinking temperature using the same pressurized fluid used to press the tyre against the walls of the molding cavity, heated to a maximum temperature of between 100 and 250°C. The time required to obtain a satisfactory degree of crosslinking throughout the mass of the elastomeric material can vary in general between 3 min and 60 min and depends mainly on the dimensions of the tyre.

A number of embodiments of the present invention are given below.

EXAMPLES 1-4

The compositions given in Table 1 were prepared using an open cylinder mixer, with a mixing time of about 30 min, keeping the maximum temperature at about 70°C.

The compositions thus prepared were subjected to MDR rheometric analysis using an MDR rheometer from Monsanto, the tests being carried out at 170°C for 30 min, with an oscillation frequency of 1.66 Hz (100 oscillations per minute) and an oscillation amplitude of ± 0.5°. Table 1 gives the parameters of the MDR curves thus obtained.

TABLE 1

EXAMPLE	1	2	3(*)	4(*)
Epoxyprene® ENR 25	100	100	100	100
Zeosil® 1165	40	60	--	--
N234	--	--	--	60
M_L (dN·m)	2.33	4.35	1.01	2.65
M_H (dN·m)	7.50	19.63	1.19	3.74
M_{fin} (dN·m)	7.50	19.63	0.74	3.74
t_{ML} (sec)	0.13	0	--	0
t_{s1} (sec)	0.31	0.07	--	23.7
t_{90} (sec)	3.57	3.22	0.10	21.8
M_{eff} (dN·m)	6.93	17.97	--	3.66
t_{eff} (sec)	0.96	0.95	--	23.9
$\%R_{eff}$	89.0	89.2	--	92.6

(*) Comparative

Epoxyprene® ENR 25: epoxidized natural rubber containing 25 mol% of epoxide groups (Guthrie);

Zeosil® 1165: precipitated silica with a BET surface area equal to 165 m^2/g and a density of hydroxyl groups equal to 13.1 groups/nm^2 (Rhône-Poulenc)

The examples given in Table 1 show that, with the compositions according to the invention containing silica, it is possible to achieve a high degree of crosslinking without the addition of any conventional crosslinking system. In contrast, using carbon black alone (essentially free of active hydroxyl groups) instead of silica, it is not possible to obtain

appreciable crosslinking in industrially acceptable times.

EXAMPLES 5-6

The compositions given in Table 2 were prepared using the same open mixer as in Examples 1-4, with a mixing time of about 30 min, the maximum temperature being kept at about 60°C.

The compositions thus prepared were subjected to MDR rheometric analysis using the same rheometer and under the same conditions as in Examples 1-4. The rheometric curves thus obtained are given in Fig. 3 (continuous line: Ex. 5, dashed line: Ex. 6), while the significant parameters are given in Table 2.

The mechanical properties (according to ISO standard 37) and the hardness in IRHD degrees (according to ISO standard 48) were measured on samples of the abovementioned compositions crosslinked at 170°C for 10 min. The results are given in Table 2.

As can be seen from the data given in Table 2, the composition according to the present invention, which is free of conventional crosslinking agents, makes it possible to obtain a crosslinked product which has characteristics that are entirely comparable with those which can be obtained by the same composition to which a conventional sulphur-based crosslinking system has been added.

TABLE 2

EXAMPLE	5	6(*)
Epoxyprene® ENR 50	100	100
Zeosil® 1165	70	70
Vulkanox® HS	1.5	1.5
Stearic acid	--	2
ZnO	--	2.5
Vulkacit® CZ	--	2
Sulphur	--	1.2
M_L (dN·m)	4.61	4.62
M_H (dN·m)	19.65	24.83
M_{fin} (dN·m)	19.65	18.81
t_{ML} (sec)	0.1	0.1
t_{s1} (sec)	0.23	0.36
t_{90} (sec)	12.06	1.64
M_{eff} (dN·m)	17.27	22.37
t_{eff} (sec)	1.75	4.71
%R_{eff}	84.2	87.8
Breaking load (MPa)	9.42	11.76
Elongation at break (%)	137	153
Hardness at 23°C (IRHD degrees)	82.9	82.6
Hardness at 100°C (IRHD degrees)	67.0	71.8

(*) Comparative

Epoxyprene® ENR 50: epoxidized natural rubber containing 50 mol% of epoxide groups (Guthrie);

Vulkanox® HS: oligomerized 2,2,4-trimethyl-1,2-dihydroquinoline (antioxidant - Bayer);

Vulkacit® CZ: N-cyclohexyl-2-benzothiazylsulphenamide (accelerator - Bayer).

EXAMPLES 7-9

Compositions consisting of 100 phr of 50% epoxidized natural rubber (Epoxyprene® ENR 50), 70 phr of silica (Zeosil® 1165) and 1.5 phr of antioxidant (Vulkanox® HS) were prepared.

For Example 7, the same open cylinder mixer as in Examples 1-4 was used, with a mixing time of about 30 min, the maximum temperature being kept at about 60°C. Example 8 was carried out using a closed mixer with interlocking rotors (Intermix), with a processing time of 20 min and a maximum temperature of 95°C. Lastly, Example 9 was carried out using a closed mixer with tangential rotors (Banbury), with a processing time of 5 min, reaching a maximum temperature of 120°C. For Examples 8 and 9, the blend was subsequently reprocessed in the open mixer for about 2 min in order to obtain a uniform sheet from which the samples for the subsequent tests were taken.

The blends thus obtained were crosslinked at 170°C for 10 min. The results are given in Table 3. For Example 9 (comparative) no data relating to the MDR curves are given since they were barely reproducible.

It is clear from these data that insufficient dispersion of the silica in the polymer matrix (Ex. 9) leads to a crosslinked product with poor tensile strength properties.

TABLE 3

EXAMPLE	7	8	9(*)
M_L (dN·m)	4.61	5.94	--
M_H (dN·m)	19.65	13.91	--
M_{fin} (dN·m)	19.65	13.91	--
t_{ML} (sec)	0.1	0	--
t_{s1} (sec)	0.23	0.16	--
t_{90} (sec)	12.06	7.67	--
M_{eff} (dN·m)	17.27	12.88	--
t_{eff} (sec)	1.75	1.11	--
%R_{eff}	84.2	87.1	--
Degree of dispersion of silica (%)	100	98.2	89.5
Breaking load (MPa)	14.3	10.9	7.2
Elongation at break (%)	143	202	118

(*) Comparative

EXAMPLES 10-14

The compositions given in Table 4 were prepared using the same open mixer as in Examples 1-4, with a mixing time of about 30 min, the maximum temperature being kept at about 60°C. Optical microscopy analysis of the compositions thus obtained showed an essentially complete dispersion of the filler. The data relating to the rheometric curves (obtained as described in Examples 1-4) are given in Table 4. The mechanical properties (according to ISO standard 37) and the crosslinking density (d_R) were measured on crosslinked samples. The crosslinking density was determined by measuring the swelling in toluene.

The results obtained demonstrate that the compositions containing a mixture of silica and carbon black as filler are capable of crosslinking effectively, provided that the silica is predominant relative to the total amount of filler added.

TABLE 4

EXAMPLE	10	11	12	13(*)	14(*)
Epoxyprene® ENR 50	100	100	100	100	100
Zeosil® 1165	60	40	30	20	10
Carbon black N234	--	18	27	36	45
M_H - M_L (dN·m)	11.47	12.25	13.59	13.42	10.70
t_{eff} (min)	2.19	2.14	2.15	1.92	1.75
$\%R_{eff}$ (%)	77.8	72.9	68.6	62.9	53.8
d_R (mol/g)	2.96×10^{-5}	2.54×10^{-5}	2.20×10^{-5}	1.87×10^{-5}	1.34×10^{-5}
Breaking load (MPa)	10.8	9.0	9.0	6.9	4.9
Elongation at break (%)	334	334	351	348	424

(*) Comparative

EXAMPLE 15

A composition consisting of 100 phr of 10% epoxidized natural rubber (Epoxyprene® ENR 10) and 70 phr of silica (Zeosil® 1165) was prepared, using the same open mixer as in Examples 1-4. The composition was crosslinked by heating to 170°C for

10 min. The following were measured on a sample of the crosslinked material:

- the hardness in IRHD degrees according to ISO standard 48;
- the modulus of elasticity E′, determined using a dynamic Inston device in traction-compression according to the following procedures.

A test piece of the crosslinked material, of cylindrical shape (length = 25 mm; diameter = 14 mm), preloaded in compression up to a longitudinal deformation of 10% relative to the initial length, and kept at 70°C throughout the test, was subjected to a dynamic sinusoidal deformation of amplitude ± 3.33% relative to the length under pre-loading, with a frequency of 100 Hz.

The results obtained are as follows:

IRHD hardness:	90 at 23°C
IRHD hardness:	84 at 100°C
Modulus of elasticity (E′) at 70°C:	30.2 MPa

The high values of hardness and of dynamic modulus of elasticity even at high temperature clearly shows that this composition is particularly suitable for constituting the filler in a tyre bead, for which an IRHD hardness at 100°C of greater than 80 and a modulus of elasticity E′ at 70°C of greater than 15 MPa are generally required.

CLAIMS

1. Process for producing tyres for the wheels of vehicles, the said process comprising the following phases:
   - making a raw tyre comprising at least one crosslinkable elastomeric material;
   - molding the raw tyre in a molding cavity defined in a vulcanization mold;
   - crosslinking the elastomeric material by heating the tyre to a predetermined temperature and for a predetermined time;

   characterized in that the raw tyre comprises at least one crosslinkable elastomeric material comprising an elastomeric polymer containing epoxide groups and an active filler containing hydroxyl groups which is dispersed in the said polymer, and in that the phase of crosslinking of the said elastomeric material is carried out essentially without additional crosslinking agents.
2. Process according to Claim 1, in which the cross-linking phase is carried out by heating the tyre to a maximum temperature of at least 100°C for a time of at least 3 minutes.
3. Process according to Claim 2, in which the cross-linking phase is carried out by heating the tyre to a maximum temperature of at least 120°C for a time of at least 5 minutes.
4. Process according to any one of the preceding claims, in which the active filler is dispersed

in the elastomeric polymer containing epoxide groups, with a dispersion index of greater than 90%.

5. Process according to Claim 4, in which the active filler is dispersed in the elastomeric polymer containing epoxide groups, with a dispersion index of greater than 95%.

6. Process according to Claim 5, in which the active filler is dispersed in the elastomeric polymer containing epoxide groups, with a dispersion index of greater than 98%.

7. Process according to any one of the preceding claims, in which the crosslinkable elastomeric material is characterized by an effective degree of crosslinking equal to at least 65% after no more than 5 min of heating at 170°C.

8. Composition comprising an elastomeric polymer containing epoxide groups and an active filler containing hydroxyl groups dispersed in the said polymer, the said composition being crosslinkable essentially without additional crosslinking agents and being characterized by an effective degree of crosslinking equal to at least 65% after no more than 5 min of heating at 170°C.

9. Composition according to Claim 8, in which the active filler is dispersed in the elastomeric polymer containing epoxide groups, with a dispersion index of greater than 90%.

10 Composition according to Claim 9, in which the active filler is dispersed in the elastomeric

polymer containing epoxide groups, with a dispersion index of greater than 95%.

11. Composition according to Claim 10, in which the active filler is dispersed in the elastomeric polymer containing epoxide groups, with a dispersion index of greater than 98%.

12. Composition according to any one of Claims 8 to 11, in which the elastomeric polymer containing epoxide groups is a homopolymer or copolymer with elastomeric properties, having a glass transition temperature (T_g) of less than 23°C.

13. Composition according to Claim 12, in which the elastomeric polymer containing epoxide groups has a glass transition temperature (T_g) of less than 0°C.

14. Composition according to any one of Claims 8 to 13, in which the elastomeric polymer contains at least 0.05 mol% of epoxide groups relative to the total number of moles of monomers present in the polymer.

15. Composition according to Claim 14, in which the elastomeric polymer contains from 0.1 to 70 mol% of epoxide groups relative to the total number of moles of monomers present in the polymer.

16. Composition according to Claim 15, in which the polymer contains from 0.5 to 60 mol% of epoxide groups relative to the total number of moles of monomers present in the polymer.

17. Composition according to any one of Claims 8 to 16, in which the elastomeric polymer has a mean molecular weight of between 2,000 and 1,000,000.
18. Composition according to Claim 17, in which the elastomeric polymer has a mean molecular weight of between 50,000 and 500,000.
19. Composition according to any one of Claims 8 to 18, in which the elastomeric polymer is an epoxidized diene homopolymer or copolymer derived from one or more conjugated diene monomers, optionally copolymerized with monovinylarenes and/or polar comonomers.
20. Composition according to Claim 19, in which the elastomeric polymer containing epoxide groups is chosen from: natural rubber, polybutadiene, polyisoprene, styrene/butadiene copolymers, butadiene/isoprene copolymers, styrene/isoprene copolymers, nitrile rubbers or mixtures thereof.
21. Composition according to any one of Claims 8 to 18, in which the elastomeric polymer is a copolymer of one or more monoolefins with an olefinic comonomer containing one or more epoxide groups.
22. Composition according to any one of Claims 8 to 21, in which the elastomeric polymer is a mixture with one or more non-epoxidized elastomeric polymers.
23. Composition according to any one of Claims 8 to 22, in which the active filler is chosen from: silica, alumina, titanium oxide, cellulose

fibres, microcrystalline cellulose, zeolites, kaolin, or mixtures thereof.

24. Composition according to Claim 23, in which the active filler is chosen from precipitated silica, pyrogenic silica, alumina, or mixtures thereof.
25. Composition according to any one of Claims 8 to 22, in which the active filler is a filler whose surface is modified with hydroxyl groups.
26. Composition according to Claim 25, in which the active filler is carbon black coated at least partially with silica.
27. Composition according to any one of Claims 8 to 26, in which the surface area of the active filler is greater than 40 m^2/g.
28. Composition according to Claim 27, in which the surface area of the active filler is between 80 and 600 m^2/g.
29. Composition according to any one of Claims 8 to 28, in which the filler has a density of active hydroxyl groups of greater than 1 group/nm^2.
30. Composition according to Claim 29, in which the filler has a density of active hydroxyl groups of greater than 5 groups/nm^2.
31. Composition according to any one of Claims 8 to 30, in which the active filler is present in an amount of greater than 20 phr.
32. Composition according to Claim 31, in which the active filler is present in an amount of between 30 and 150 phr.

33. Composition according to any one of Claims 8 to 32, in which the active filler is a mixture with a non-active reinforcing filler.
34. Composition according to Claim 33, in which the active filler is at least 50% by weight of the total filler present in the composition.
35. Composition according to any one of Claims 8 to 34, also comprising one or more additives chosen from: antioxidants, protective agents, plasticizers, adhesives, anti-ozonizing agents, curing resins, modifying resins, fibres and the like.
36. Composition according to any one of Claims 8 to 35, also comprising a lubricant.
37. Composition according to Claim 36, in which the lubricant is present in an amount of between 2 and 100 phr.
38. Composition according to Claim 37, in which the lubricant is present in an amount of between 5 and 50 phr.
39. Process for preparing an elastomeric composition comprising an elastomeric polymer containing epoxide groups and an active filler containing hydroxyl groups which is dispersed in the said polymer, the said composition being crosslinkable without additional crosslinking agents, the said process comprising mixing the active filler with the polymer for a predetermined time so as to obtain a degree of dispersion of the filler of greater than 90%, and at a predetermined

temperature so as to avoid pre-crosslinking of the composition.

40. Process according to Claim 39, in which the mixing temperature is kept below 130°C.

41. Process according to Claim 40, in which the mixing temperature is kept below 100°C.

42. Process according to Claim 41, in which the mixing temperature is kept below 80°C.

43. Process according to any one of Claims 39 to 42, in which the active filler and the polymer are mixed using an open mixer.

44. Process according to any one of Claims 39 to 42, in which the active filler and the polymer are mixed using an internal mixer.

45. Process according to any one of Claims 39 to 42, in which the active filler and the polymer are mixed using a continuous mixer.

46. Process according to any one of Claims 43 to 45, in which the mixing time is greater than 90 sec.

47. Process according to any one of Claim 46, in which the mixing time is between 3 and 35 min.

48. Process according to any one of Claims 39 to 42, in which the active filler is mixed with the polymer base in the form of an aqueous emulsion or a solution in an organic solvent, and the polymer containing the dispersed filler is then separated out by precipitation.

49. Crosslinked manufactured product comprising an elastomeric polymer containing epoxide groups and an active filler containing hydroxyl groups which

is dispersed in the said polymer, characterized in that the said manufactured product is crosslinked essentially without additional crosslinking agents, and the filler is dispersed in the polymer, with a dispersion index of greater than 90%.

50. Manufactured product according to Claim 49, in which the active filler is dispersed in the elastomeric polymer containing epoxide groups, with a dispersion index of greater than 95%.

51. Manufactured product according to Claim 50, in which the active filler is dispersed in the elastomeric polymer containing epoxide groups, with a dispersion index of greater than 98%.

52. Manufactured product according to any one of Claims 49 to 51, which is obtained by crosslinking, essentially without additional crosslinking agents, a composition according to any one of Claims 8 to 38.

53. Tyre for the wheels of vehicles, comprising one or more components made of crosslinked elastomeric material, characterized in that at least one of the said components comprises a crosslinked elastomeric material comprising an elastomeric polymer containing epoxide groups and an active filler containing hydroxyl groups dispersed in the said polymer, the said material being crosslinked essentially without additional crosslinking agents.

54. Tyre according to Claim 53, in which the crosslinked elastomeric material is obtained by crosslinking, essentially without additional crosslinking agents, a composition according to any one of Claims 8 to 38.

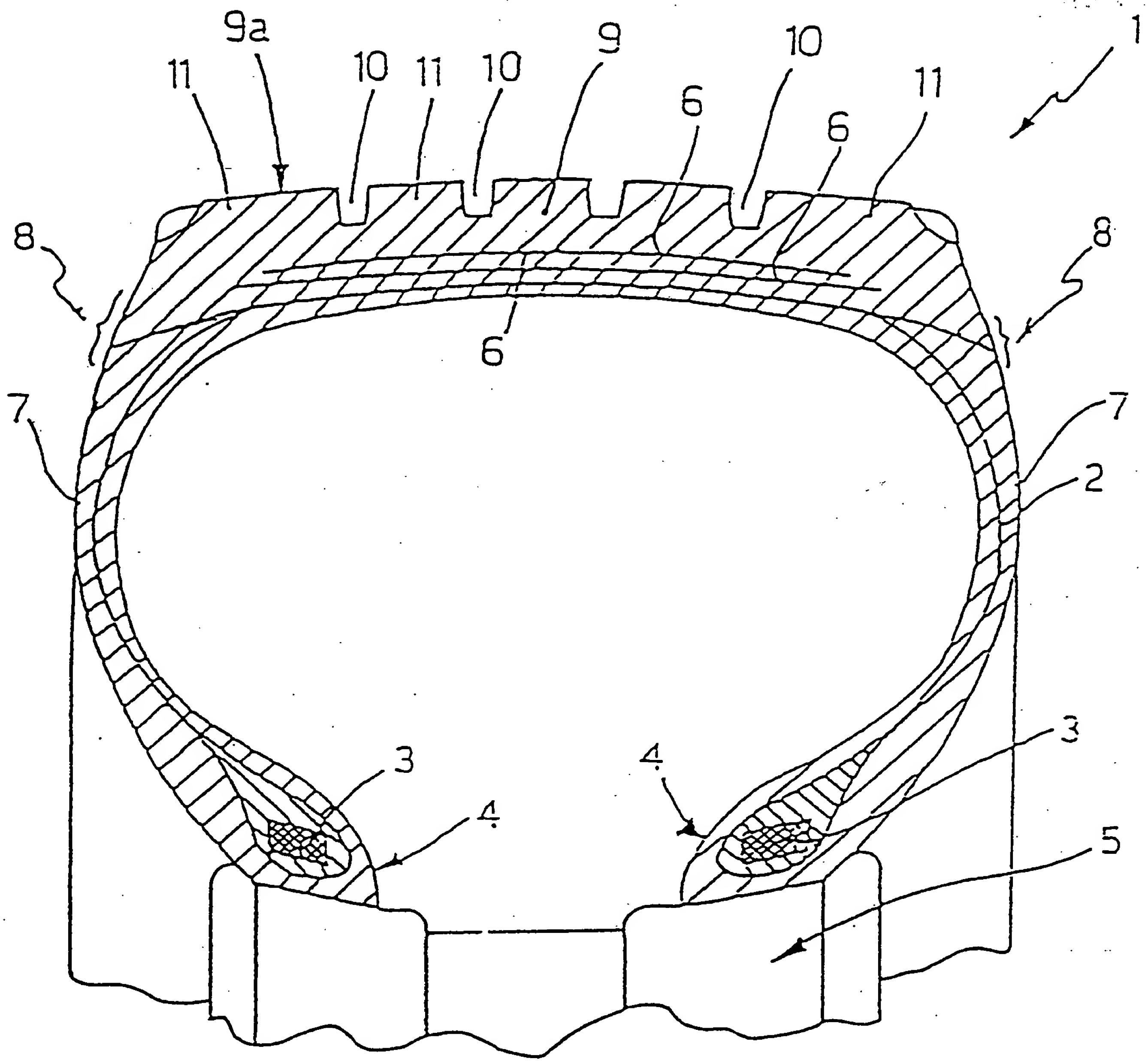

FIG. 1

FIG. 2

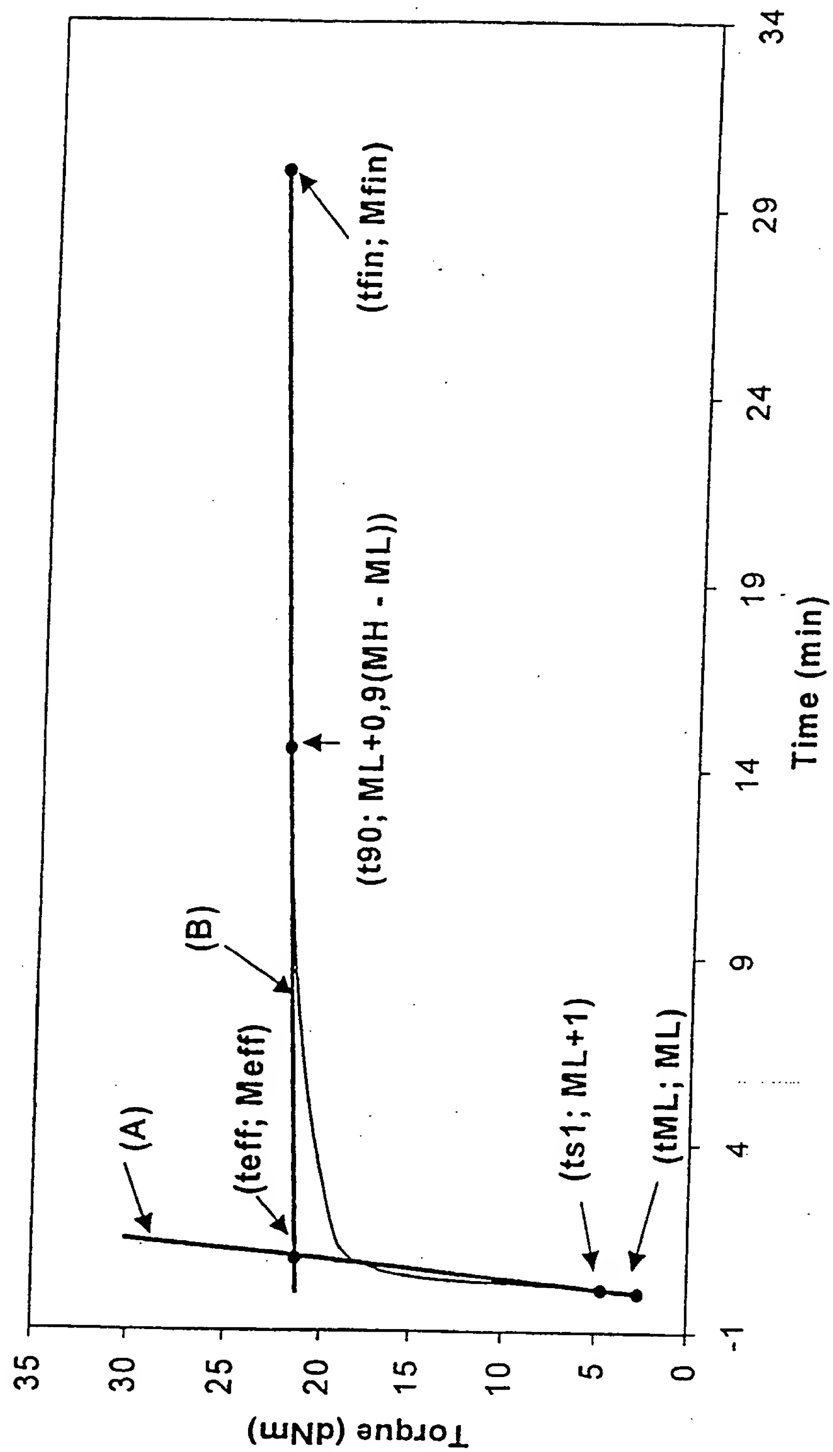
(A)
(teff; Meff)
(B)
(t90; ML+0,9(MH - ML))
(tfin; Mfin)
(ts1; ML+1)
(tML; ML)
Torque (dNm)
35
30
25
20
15
10
5
0
-1
4
9
14
19
24
29
34
Time (min)

FIG. 3